



# Chemical modeling for pH prediction of acidified musts with gypsum and tartaric acid in warm regions



J. Gómez<sup>a,\*</sup>, C. Lasanta<sup>a</sup>, J.M. Palacios-Santander<sup>b</sup>, L.M. Cubillana-Aguilera<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, Food Technology, Faculty of Sciences, Campus Río San Pedro, PB 40, Puerto Real, University of Cadiz 11510, Spain

<sup>b</sup> Department of Analytical Chemistry, Faculty of Sciences, Campus Río San Pedro, PB 40, Puerto Real, University of Cadiz 11510, Spain

## ARTICLE INFO

### Article history:

Received 17 April 2014

Received in revised form 23 June 2014

Accepted 7 July 2014

Available online 15 July 2014

### Keywords:

Acidification

Gypsum

Plastering

Tartaric acid

Musts

Chemical modeling

pH prediction

Buffering power

## ABSTRACT

Winemaking of musts acidified with up to 3 g/L of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and tartaric acid, both individually and in combination, as well as a chemical modeling have been carried out to study the behaviour of these compounds as acidifiers. Prior to fermentation gypsum and tartaric acid reduce the pH by 0.12 and 0.17 pH units/g/L, respectively, but while gypsum does not increase the total acidity and reduces buffering power, tartaric acid shows the opposite behaviour. When these compounds were used in combination, the doses of tartaric acid necessary to reach a suitable pH were reduced. Calcium concentrations increase considerably in gypsum-acidified must, although they fell markedly after fermentation over time. Sulfate concentrations also increased, although with doses of 2 g/L they were lower than the maximum permitted level (2.5 g/L). Chemical modeling gave good results and the errors in pH predictions were less than 5% in almost all cases.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

The acidification of musts has the objective of reducing their pH to suitable values in order to inhibit bacterial activity, stabilize the colour and improve the sensorial characteristics of the resulting wines (Ribereau-Gayon, Dubourdieu, Doneche, & Lonvaud, 2006). The intensity of the acidic taste of wines is directly related to the pH and its length with the buffering power (Plane, Mattick, & Weirs, 1980). Acidification of musts is necessary in warm areas where high temperatures during ripening accelerate breathing combustion of tartaric acid and, in particular, malic acid in the berries (Harris, Kriedermann, & Possingham, 1971; Ruffner, Brem, & Rast, 1983). L(+)-tartaric acid has traditionally been the only acidification agent used to date but the latest regulations of the European Union also authorise the use of L-malic acid, D,L-malic acid and lactic acid (European Community, 2008; European Community, 2009). The maximum authorised doses are 1.5 g/L in grape juice and 2.5 g/L in wine, expressed as tartaric acid. The use of calcium sulfate (gypsum:  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is also authorised as a complementary acidifier in generous and generous liquor wines from Spain (a practice known as plastering) provided that the residual sulfate content in the wine does not exceed 2.5 g/L

expressed as potassium sulfate. Calcium sulfate is also authorised in the United States for the production of wines aged under yeast veil but residual sulfate cannot exceed 2 g/L (e-CFR.Electronic Code of Federal Regulations., 2010). Plastering is a practice that has its roots in history (Plinius Maior, 1st Century) and this approach has traditionally been used in Sherry (Fernández de Bobadilla, Quirós, & Serrano, 1954; Gonzalez-Gordon, 1972; Jeffs, 1982) and Port winemaking (Pato, 1971). Fernández de Bobadilla et al. (1954) found that a dose of 3 g/L of plaster leads to a reduction in pH of 0.2 units in Sherry musts prior to fermentation. Gomez Benitez, Grandal Delgado, and Diez Martin (1993) recommended a combined acidification with 2 g/L of gypsum and sufficient tartaric acid to achieve a pH of 3.25. In this way, the necessary dose of tartaric acid does not exceed 1.5 g/L, the maximum authorised level, and the final concentration of sulfates is lower than 2.5 g/L. More recently, (Casas Lucas, 2008) proposed a semiempirical method to calculate the doses of gypsum and tartaric acid required to reduce the pH of the musts to 3.40.

Several chemical modeling approaches have been described in the literature with the aim of predicting the effect of acidification on pH and the general acid-base properties and ionic strength in white and red wines. Boulton (1980) proposed a simple model in which the pH is expressed as a function of the titratable acidity, the potassium and sodium contents and the tartrate to malate ratio. A very complex model was also proposed that employs 13

\* Corresponding author. Tel.: +34 956016382; fax: +34 956016411.

E-mail address: [juangomez.benitez@uca.es](mailto:juangomez.benitez@uca.es) (J. Gómez).

organic acids, 4 inorganic anions, 5 metal cations, protonation constants, different alcohol contents for white wines and 14 acid-base active substances and 22 protonation equilibria for red wines (Prenesti, Berto, Toso, & Daniele, 2012; Prenesti, Toso, Daniele, Zelano, & Ginepro, 2004). Moreno Vigara and Peinado Amores (2010) updated and improved the model proposed by (Usseglio-Tomasset, 1995) and developed a model that was much simpler and easier to apply. In this model the acidity of wine is considered to be due to a monoprotic acid. The dissociation of the acid can be represented as follows:



The acidity constant would be

$$K_V = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} \quad (2)$$

and

$$\text{p}K_V = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (3)$$

which can be written as

$$\text{p}K_V = \text{pH} - \log \frac{\text{AA}}{\text{TA}} \quad (4)$$

where TA is total acidity and AA is ash alkalinity.

The buffering power of the must depends on the concentration of the various ionic forms of tartaric acid in accordance with the following expression:

$$\pi = \text{Buffering power} = \frac{d\text{Ac}}{d\text{pH}} = 2.303 \frac{[\text{HA}][\text{A}^-]}{[\text{HA}] + [\text{A}^-]} \quad (5)$$

which can be simplified as

$$\pi = \text{Buffering power} = \frac{d\text{Ac}}{d\text{pH}} = 2.303 \frac{[\text{TA}][\text{AA}]}{[\text{TA}] + [\text{AA}]} \quad (6)$$

Buffering power can be easily determined in the laboratory and allows the calculation of AA

$$\text{AA} = \frac{\pi \times \text{TA}}{2.303 \times \text{TA} - \pi} \quad (7)$$

All of these approximations can be applied since the variation of pH is considered to be infinitesimal.

The effect on pH of adding X meq/L of tartaric acid can be predicted by considering that

$$\text{TA}_f = \text{TA}_i + 2X \quad (8)$$

and

$$\text{AA}_f = \text{AA}_i \quad (9)$$

where the subscripts 'i' and 'f' denote initial and final, respectively.

In this way

$$\text{pH}_f = \text{p}K_V + \log \frac{\text{AA}_f}{\text{TA}_f} = \text{p}K_V + \log \frac{\text{AA}_i}{\text{TA}_i + 2X} \quad (10)$$

After the addition of tartaric acid a precipitation of X meq/L of potassium bitartrate will occur and AA and TA will be modified as follows:

$$\text{AA}_f = \text{AA}_i - X \quad (11)$$

and

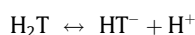
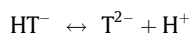
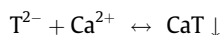
$$\text{TA}_f = \text{TA}_i + 2X - X = \text{TA}_i + X \quad (12)$$

And the final pH would be calculated as:

$$\text{pH} = \text{p}K_V + \log \frac{\text{AA}_f}{\text{TA}_f} = \text{p}K_V + \log \frac{\text{AA}_i - X}{\text{TA}_i + X} \quad (13)$$

In this model it is considered that the medium is saturated in tartrate and, as a consequence, the addition of tartaric acid as an acidifying agent will introduce the common ion  $\text{HT}^-$  and this will precipitate naturally or during cold stabilization as potassium bitartrate. In this way, one can consider that all of the  $\text{HT}^-$  added will precipitate as potassium bitartrate and this does not contribute to the titratable acidity (Moreno Vigara & Peinado Amores, 2010).

The effect of  $\text{CaSO}_4$  in grape must is based on the displacement of the ionic equilibrium produced by the  $\text{Ca}^{2+}$  ion. The equilibria of two salts with limited solubility are involved in this case, namely  $\text{CaSO}_4$  ( $K_{SP} = 6.1 \cdot 10^{-5}$ ) and calcium tartrate [ $\text{Ca}(\text{C}_4\text{H}_4\text{O}_6$ ), hereafter CaT] ( $K_{SP} = 7.7 \cdot 10^{-7}$ ).  $\text{CaSO}_4$  dissolves up to the solubility products of the  $\text{CaSO}_4$  and CaT. As the latter species is much less soluble than the former, the precipitation of CaT occurs. However, on decreasing the concentration of one of the ionic forms of tartaric acid (hereafter  $\text{H}_2\text{T}$ ), a redistribution of the other occurs and, in accordance with the dissociation constants of this acid ( $K_1 = 1.04 \cdot 10^{-3}$ ;  $K_2 = 4.55 \cdot 10^{-5}$ ) and to replace the removed tartrate ion (hereafter  $\text{T}^{2-}$ ), a proportion of the bitartrate ion (thereafter  $\text{HT}^-$ ) is dissociated and this in turn is replaced by another tartrate from the dissociation of  $\text{H}_2\text{T}$ . The different ionic reactions considered are as follows:



which gives rise to the following global reaction:



The release of these two protons leads to a decrease in the pH of the must.

The addition of Y meq/L of  $\text{CaSO}_4$  removes Y meq/L of tartrate and AA and TA will also decrease to the same extent. Therefore:

$$\text{AA}_f = \text{AA}_i - Y \quad (15)$$

$$\text{TA}_f = \text{TA}_i - Y \quad (16)$$

The buffering power will be affected differently depending on whether the acidification is carried out with gypsum or tartaric acid. The increase in the fraction [HA] on adding tartaric acid should affect the numerator rather than the denominator in Eq. (6), thus causing an increase in the buffering power. Similarly, the decrease of  $[\text{A}^-]$  caused by the addition of gypsum will cause a decrease in the buffering power.

The aim of the work described here was to expand on the procedure described by Gomez Benitez et al. (1993), for the vinification of musts and acidified musts with gypsum and tartaric acid, added either individually and in combination, using doses up to 3 g/L and to study the modifications that these practices produce on the compositions of the resulting wines. At the same time, chemical modeling of the acid-base and precipitation equilibria was carried out to calculate pH values and compare them with the experimental ones in order to verify the applicability of the hypothesis in which the acidity of wine is considered to be caused by a monoprotic acid. To our knowledge, this is the first time that this kind of simplified modeling has been carried out with real data, mainly for the combined addition of gypsum and tartaric acid. Through these studies the traditional practice of plastering will be explained and evidence will be provided to support this process.

## 2. Materials and methods

### 2.1. Description of the winemaking process

The must was obtained in a winery in the Jerez area (Southern Spain) from *Vitis vinifera* L. cv. Palomino Fino grapes pressed at less than 1.0 bar and sulfited with 100 mg/L of SO<sub>2</sub>.

### 2.2. Reagents

All laboratory reagents were of analytical grade. For HPLC analysis the reagents used were HPLC grade. The water for the preparation of solutions and controls was distilled and purified by reverse osmosis (Millipore Milli-Q Plus TM). Gypsum and tartaric acid were food quality. Gypsum was prepared as a suspension of 500 g/L continuously stirred to prevent setting. H<sub>2</sub>T was prepared as a solution of 500 g/L.

### 2.3. Description of the pilot scale tests

The pilot scale tests were carried out in 25 L stainless steel tanks, where musts were acidified with gypsum and/or with H<sub>2</sub>T and mixed with a paddle stirrer for 5 min. After a settling period of 12 h the clear musts were drained to glass demijohns of 16 L and inoculated with active dry yeast (ADY) *Saccharomyces cerevisiae* (previously rehydrated). The musts were fermented in a thermostatic chamber at 25 °C.

### 2.4. Description of the industrial scale tests

The industrial scale tests were carried out in 30,000 L resin-coated concrete tanks, to which the acidifiers were added after filling of the tank. The mixture was stirred with pressurised nitrogen gas. The musts were settled for 12 h at ambient temperature and 17,000 L of clear must from each tank were transferred to 20,000 L stainless steel tanks and fermented at 25 °C with an inoculum of selected ADY *S. cerevisiae*.

### 2.5. Sample preparation

Samples before fermentation were taken 1 h after acidification to allow equilibria to be reached. Samples after fermentation were taken fifteen days after the end of alcoholic fermentation. An additional sampling 2 months after the end of fermentation was taken in pilot tests but not in the industrial tests due to operational requirements. All samples were centrifuged and the fermented ones were also subjected to ultrasound degassing to remove CO<sub>2</sub>. The samples were filtered through an 8 µm membrane. Samples to be analysed by HPLC were also filtered through a 0.22 µm membrane. All of the tests and determinations were performed in duplicate and average values are given in the tables.

### 2.6. Analytical methods

Alcoholic strength, pH, total acidity, potassium, calcium and sulfates were analysed by the official European Union analysis methods (European Community, 1990). Buffering power was determined by titration until pH = 3 with 0.1 N HCl. The results are expressed in meq/L pH unit. Tartaric acid was determined by HPLC (Frayne, 1986).

### 2.7. Equipment

pH-meter: Orion Research Model 811. Atomic absorption spectrophotometer: Perkin-Elmer Model 372. Liquid chromatograph:

Waters with a 990 photodiode-array detector. Four Waters Fast Fruit TM chromatographic columns and one IC-PAK TM ion exclusion column connected in series were used. Detection was performed at 214 nm.

### 2.8. Modeling

In order to obtain a chemical model to predict pH values from experimentally measured analytical data, total acidity (TA), ash alkalinity (AA) and pK<sub>v</sub> values were calculated: TA by simple direct conversion and AA and pK<sub>v</sub> using Eqs. (7) and (4), respectively. All calculations and modeling were carried out with Microsoft Office Excel 2010.

## 3. Results and discussion

### 3.1. Acidifier behaviour of gypsum at pilot scale

As can be seen from the results in Table 1, the addition of gypsum reduces the pH of the must before fermentation by a magnitude that is directly related to the dose, which for 3 g/L is 0.12 units/g on average. The total acidity does not increase because new H<sup>+</sup> ions are not created and the tartaric acid concentration and buffering power decrease due to CaT precipitation. The calcium concentration increases markedly due to the addition of CaSO<sub>4</sub>·2H<sub>2</sub>O and the potassium concentration does not change. After fermentation, a significant KHT precipitation had occurred due to the formation of ethanol, as shown by the decreases in tartaric acid and potassium concentrations. These decreases are directly related to initial pH due to the relationship between % TH<sup>−</sup> and pH. However, it is necessary to take in account the fact that the pH would decrease or increase depending on whether this pH is lower or high than the pH at which the TH<sup>−</sup> ion reaches its maximum concentration (see Fig. 1). At the same time, the reduction in pH and increase in total acidity observed can be justified by the fact that the formation of new acids during fermentation (Shimazu & Watanabe, 1981) is greater than the reduction produced by KHT precipitation. Two months after fermentation an additional KHT precipitation led to increases in pH values and reductions in total acidity, both by a magnitude that is in relation to the initial pH. Finally, calcium concentrations dropped from high initial values of around 200 mg/L to more suitable final values of around 100 mg/L.

As far as pH modeling is concerned, the addition of gypsum leads to decreases in AA and TA due to precipitation of CaT and the considerations related to Eqs. (15) and (16) were taken into account. Therefore, the chemical model used to predict the pH values for the addition of gypsum alone (Moreno Vigara & Peinado Amores, 2010) is:

$$\text{pH} = \text{pK}_v + \log \frac{\text{AA}_f}{\text{TA}_f} = \text{pK}_v + \log \frac{\text{AA}_i - Y}{\text{TA}_i - Y} \quad (17)$$

where Y is the dose of CaSO<sub>4</sub> in meq/L.

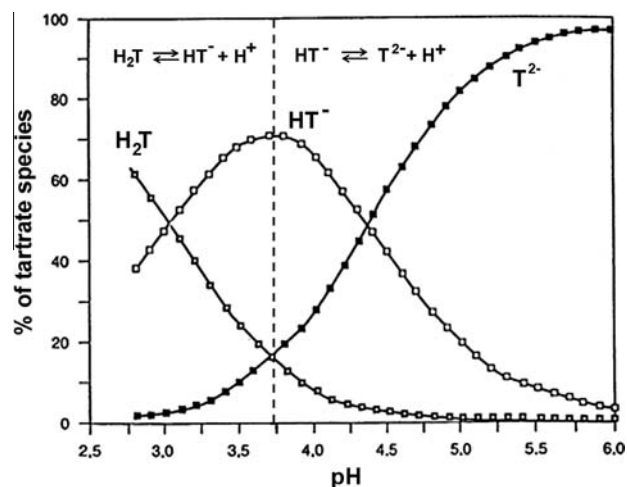
As can be seen from the results in Table 1, this model provides a very good prediction of experimental pH values during all of the studied fermentation steps. The fitting is very good and the relative errors are below 2%. Hence, in this case, the theory is in good agreement with pilot scale experimental results.

### 3.2. Acidifier behaviour of tartaric acid at pilot scale

The addition of tartaric acid also reduces the pH of must in relation to the dose. For a dose of 3 g/L the pH is reduced by 0.17 units/g on average with consequent increases in total acidity and buffering power (Table 2). The tartaric acid concentrations do not increase at the same rate as a result of KHT precipitation induced

**Table 1**  
Acidification with gypsum at pilot scale.

State	Gypsum dose (g/L)		pH	Total acidity (g/L H <sub>2</sub> T)	Calcium (mg/L)	Sulphates (g/L K <sub>2</sub> SO <sub>4</sub> )	Potassium (mg/L)	Tartaric acid (g/L)	Buffering power (meq/L u pH)	TA (meq/L)	AA (meq/L)	pK <sub>v</sub>	Calculated pH <sup>3</sup>	Relative error (%)
	CaSO <sub>4</sub>	2 H <sub>2</sub> O												
Before AF <sup>1</sup>	0.00	0.00	3.79	3.67	175	nd <sup>2</sup>	2018	6.385	38.57	48.93	25.46	4.07	3.79	0.10
	1.00	0.79	3.67	3.60	190	nd <sup>2</sup>	2018	5.615	34.74	48.00	22.00	4.01	3.73	1.60
	2.00	1.58	3.53	3.67	200	nd <sup>2</sup>	2018	4.99	32.92	48.93	20.19	3.91	3.59	1.81
	3.00	2.37	3.41	3.60	270	nd <sup>2</sup>	2009	4.44	31.03	48.00	18.73	3.82	3.43	0.68
After AF <sup>1</sup>	0.00	0.00	3.57	3.74	40	0.53	1400	3.97	35.30	49.87	22.13	3.92	3.57	0.08
	1.00	0.79	3.49	3.82	65	1.61	1567	3.865	34.70	50.93	21.40	3.87	3.49	0.04
	2.00	1.58	3.38	4.36	100	2.60	1800	4.08	33.20	58.13	19.17	3.86	3.41	0.84
	3.00	2.37	3.28	4.48	120	3.59	1900	4.09	32.80	59.73	18.70	3.78	3.27	0.39
2 months after AF <sup>1</sup>	0.00	0.00	3.69	3.56	40	0.50	950	1.98	30.40	47.47	18.29	4.10	3.69	0.12
	1.00	0.79	3.58	3.39	65	1.50	1150	1.85	27.60	45.20	16.31	4.02	3.58	0.10
	2.00	1.58	3.42	3.70	97	2.52	1400	1.86	26.10	49.33	14.71	3.95	3.45	0.75
	3.00	2.37	3.27	3.99	110	3.45	1550	1.91	26.70	53.20	14.82	3.82	3.26	0.28

<sup>1</sup> AF: alcoholic fermentation.<sup>2</sup> nd: not determined.<sup>3</sup> Calculations carried out according to Eq. (17).**Fig. 1.** Variation of H<sub>2</sub>T, HT<sup>-</sup> and T<sup>2-</sup> concentrations in wine according to pH. H<sub>2</sub>T: undissociated tartaric acid; HT<sup>-</sup>: bitartrate ion; T<sup>2-</sup>: tartrate ion.

by the addition of H<sub>2</sub>T. After fermentation, a significant KHT precipitation occurs and this leads to a reduction in the total acidity of wines by a magnitude that is related to the dose of H<sub>2</sub>T used, despite the formation of new acids. Two months later, KHT precipitation continues and there is a consequent increase in pH and reductions in total acidity, tartaric acid, potassium concentrations and buffering power.

With respect to the pH modeling, Eq. (13) is employed in this case. TA, AA and pK<sub>v</sub> were calculated in a similar way to the previous case. As discussed above, this model takes into consideration acidification plus precipitation of bitartrate; hence, these assumptions can be translated into the model in the following terms: a decrease in AA and an increase in TA, according to the amount of tartaric acid added (X meq/L).

As can be seen from the results in Table 2, good agreement is again observed between experimental and calculated pH values. In general, the relative errors are very low (less than 3%) and this can be considered to be a very good result.

### 3.3. Acidifier behaviour of mixed gypsum and tartaric acid at pilot scale

The fact that all final pH values before fermentation are the same for all samples means that changes in all of the parameters depend on the doses of gypsum and tartaric acid used in each case (Table 3). After fermentation, the pH values were the same in all wines and this finding can be explained because the addition of gypsum reduces the buffering power, which leads to a variation in pH and compensates for the KHT precipitation. In contrast to the situation described in Sections 3.1 and 3.2, the pH continues to decrease 2 months later because the low pH values are close to the pK<sub>a1</sub> of tartaric acid (3.01) and this increases the evolution of the pH values. In any case, this fact favours the acidifying effect of gypsum.

The chemical models that have appeared in the literature to date (Moreno Vigara & Peinado Amores, 2010) are very useful to predict pH values at different stages of the fermentation process of musts and wines at pilot scale in cases where only one acidifier is used. However, the simultaneous addition of two acidifiers in combination leads to a different situation that is certainly more complex to model.

In our case, different doses of gypsum were added and tartaric acid was added to provide a decrease in pH to approximately 3.25. Hence, it can be seen from the results in Table 3 that the

**Table 2**  
Acidification with tartaric acid at pilot scale.

State	H <sub>2</sub> T dose (g/L)	pH	Total acidity (g/L H <sub>2</sub> T)	Calcium (mg/L)	Sulphates <sup>2</sup> (g/L K <sub>2</sub> SO <sub>4</sub> )	Potassium (mg/L)	Tartaric acid (g/L)	Buffering power (meq/L u pH)	TA (meq/L)	AA (meq/L)	pK <sub>v</sub>	Calculated pH <sup>3</sup>	Relative error (%)
Before AF <sup>1</sup>	0	3.79	3.67	175	nd	2018	6.385	38.57	48.93	25.46	4.07	3.79	0.10
	1	3.58	4.57	135	nd	1933	6.74	43.72	60.93	27.58	3.92	3.60	0.53
	2	3.43	5.47	150	nd	1766	7.19	47.8	72.93	29.01	3.83	3.41	0.57
	3	3.29	6.60	155	nd	1666	7.53	54.57	88.00	32.43	3.72	3.28	0.36
	4.05	3.24	7.65	165	nd	1566	8.115	60.98	102.00	35.76	3.70	3.15	2.63
After AF <sup>1</sup>	0	3.57	3.74	40	0.53	1400	3.97	35.30	49.87	22.13	3.92	3.57	0.08
	1	3.42	4.25	55	0.54	1267	4.3	37.30	56.67	22.68	3.82	3.36	1.84
	2	3.31	4.81	60	0.44	1134	4.815	39.40	64.13	23.33	3.75	3.22	2.63
	3	3.17	5.51	70	0.48	1067	5.675	43.70	73.47	25.58	3.63	3.12	1.52
	4.05	3.13	6.40	90	0.49	1033	6.155	48.90	85.33	28.27	3.61	3.00	4.06
2 months after AF <sup>1</sup>	0	3.69	3.56	40	0.50	950	1.98	30.40	47.47	18.29	4.10	3.69	0.12
	1	3.51	3.84	45	0.53	950	2.54	31.20	51.20	18.42	3.95	3.43	2.23
	2	3.37	4.22	55	0.47	800	2.79	31.10	56.27	17.77	3.87	3.26	3.33
	3	3.21	5.07	60	0.47	700	3.35	36.50	67.60	20.70	3.72	3.12	2.91
	4.05	3.09	5.90	65	0.48	650	3.97	40.00	78.67	22.29	3.64	3.00	3.03

<sup>1</sup> AF: alcoholic fermentation.

<sup>2</sup> nd: not determined.

<sup>3</sup> Calculations carried out according to Eq. (13).

**Table 3**  
Acidification with gypsum and tartaric acid at pilot scale.

State	Gypsum dose (g/L)		H <sub>2</sub> T Dose (g/L)	pH	Total acidity (g/L H <sub>2</sub> T)	Calcium (mg/L)	Sulphates <sup>2</sup> (g/L K <sub>2</sub> SO <sub>4</sub> )	Potassium (mg/L)	Tartaric acid (g/L)	Buffering power (meq/L u pH)	TA (meq/L)	AA (meq/L)	pK <sub>v</sub>	Calculated pH <sup>3</sup>	Relative error (%)
	CaSO <sub>4</sub> 2 H <sub>2</sub> O	CaSO <sub>4</sub>													
Before AF <sup>1</sup>	0.00	0.00	0	3.79	3.67	175	nd	2018	6.385	38.57	48.93	25.46	4.07	3.79	0.10
	1.00	0.79	3.22	3.25	6.82	245	nd	1919	8.045	53.75	90.93	31.40	3.71	3.21	1.09
	2.00	1.58	2.45	3.24	5.92	270	nd	2000	7.18	48.57	78.93	28.78	3.68	3.26	0.67
	3.00	2.37	1.3	3.24	4.87	425	nd	2027	6.19	40.71	64.93	24.29	3.67	3.39	4.59
After AF <sup>1</sup>	0.00	0.00	0	3.57	3.74	40	0.53	1400	3.97	35.30	49.87	22.13	3.92	3.57	0.08
	1.00	0.79	3.22	3.12	5.85	130	1.55	1234	5.66	43.90	78.00	25.23	3.61	2.88	7.73
	2.00	1.58	2.45	3.13	5.75	190	2.43	1467	5.405	42.30	76.67	24.15	3.63	3.08	1.63
	3.00	2.37	1.3	3.13	5.39	200	3.50	1800	4.835	39.60	71.87	22.60	3.63	3.25	3.77
2 months after AF <sup>1</sup>	0.00	0.00	0	3.69	3.56	40	0.50	950	1.98	30.40	47.47	18.29	4.10	3.69	0.12
	1.00	0.79	3.22	3.08	5.70	115	1.43	850	3.29	37.40	76.00	20.65	3.65	2.68	12.88
	2.00	1.58	2.45	3.08	5.27	152	2.39	1050	3.05	35.50	70.27	19.75	3.63	2.99	2.79
	3.00	2.37	1.3	3.07	4.94	177	3.22	1350	2.56	32.10	65.87	17.68	3.64	3.26	6.21

<sup>1</sup> AF: alcoholic fermentation.

<sup>2</sup> nd: not determined.

<sup>3</sup> Calculations carried out according to Eq. (18).



**Table 4**  
Acidification with gypsum and tartaric acid at industrial scale.

State	Gypsum dose (g/L)		H <sub>2</sub> T dose (g/L)	pH	Total acidity (g/L H <sub>2</sub> T)	Calcium (mg/L)	Sulphates <sup>2</sup> (g/L K <sub>2</sub> SO <sub>4</sub> )	Potassium (mg/L)	Tartaric acid (g/L)	Buffering power (meq/L u pH)	TA (meq/L)	AA (meq/L)	pK <sub>v</sub>	Calculated pH <sup>3</sup>	Relative error (%)
	CaSO <sub>4</sub>	2H <sub>2</sub> O													
Before AF <sup>1</sup>	0.00	0.00	0.00	3.71	3.52	120	nd	1978	7.43	39.95	46.93	27.52	3.94	3.71	0.05
	2.00	1.58	0.00	3.54	3.65	160	nd	1958	6.27	34.45	48.67	21.60	3.89	3.59	1.51
	0.00	0.00	3.52	3.23	6.58	132	nd	1793	8.90	53.84	87.73	31.87	3.67	2.63	18.67
	2.00	1.58	1.60	3.25	5.36	250	nd	1944	7.03	40.94	71.47	23.66	3.73	3.63	11.82
After AF <sup>1</sup>	2.00	1.58	0.00	3.36	4.46	130	2.51	1800	3.36	32.20	59.47	18.28	3.87	3.59	6.95
	0.00	0.00	3.52	3.11	6.05	122	0.60	1333	3.11	50.75	80.67	30.32	3.53	2.63	15.54
	2.00	1.58	1.60	3.18	5.29	162	2.53	1633	3.18	38.50	70.53	21.91	3.69	3.63	14.28

<sup>1</sup> AF: Alcoholic fermentation.<sup>2</sup> nd: not determined.<sup>3</sup> Calculations carried out according to Eq. (18).

higher the amount of gypsum present, the lower the amount of tartaric acid, and vice versa. The model was built in a similar way to those in the two previous cases. The parameters employed were TA, AA and pK<sub>v</sub>, which are based on the analytical measurements. According to the results in Table 3, TA and AA decrease in all cases, but at a higher rate prior to fermentation, while pK<sub>v</sub> remains almost constant. The chemical model employed is shown in Eq. (18):

$$\text{pH} = \text{pK}_v + \log \frac{\text{AA}_f}{\text{TA}_f} = \text{pK}_v + \log \frac{\text{AA}_i + Y - X}{\text{TA}_i + X} \quad (18)$$

With respect to the model, it should be noted that this is not a direct combination of Eqs. (13) and (17), as one might expect, and the changes mainly concern the denominator, where the contribution of Y meq/L of gypsum has been removed. Considering the numerator, the simple combination gives rise to some trends in the relative error values obtained that are not mathematically acceptable and also lead to some infinite errors (negative value) due to the nature of the data. For these reasons, some empirical changes (mathematical signs) were included in the final model (Eq. (18)) in order to avoid these problems. With respect to the denominator, and according to the experimental data (see Table 3), the contribution of gypsum to total acidity is almost negligible, as this factor is principally due to the addition of tartaric acid ( $\text{TA}_{\text{sample}} \approx \text{TA}_{\text{blank}} + \text{H}_2\text{T dose}$ , in g/L). It can be concluded from the results obtained with Eq. (18) that, in general, the relative errors are rather good, i.e., below 6%, with only two main exceptions for the highest doses of tartaric acid; this fact can be justified because the pH values are very close to pK<sub>a1</sub>, which could be considered as a critical point in the acid dissociation equilibria (Fig. 1). Therefore, the model presented here, despite its simplicity, seems to be of great interest for the prediction and control of pH after combining the addition of gypsum and tartaric acid at pilot scale, regardless of the fermentation stage.

It would be possible to enhance the model but this would certainly involve a more complex and/or more empirical approach, such as a probabilistic one (Sturm et al., 2014).

### 3.4. Acidifier behaviour of gypsum and tartaric acid at industrial scale

Following the same approach as for the pilot scale, set amounts of gypsum and tartaric acid, both separately and in combination, were added to musts before fermentation at the industrial scale. The analytical parameters measured, along with the calculated pH values and relative errors obtained, are collected in Table 4. In this case, the results are not as good as those obtained for the pilot scale, as one might expect. The models employed were those mentioned in the previous cases and these were specifically developed for pilot scale. It has to be taken into consideration that the control of the behaviour of chemical equilibria on an industrial scale is definitively more complicated than on a pilot scale, mainly due to the difference in volume (25 vs 30,000 L) and the difficulty in achieving complete homogenisation of the media after adding gypsum, tartaric acid or both. However, it should be noted that, despite these drawbacks, the results are reasonably good and, in general, the errors are less than 14% apart from the cases where tartaric acid is added to the tanks – for the same reasons as explained above.

## 4. Conclusions

The addition of gypsum leads to a reduction in pH of 0.12 pH units/g/L without an increase in total acidity and a reduction in the buffering power. The addition of tartaric acid reduces the pH by 0.17 pH units/g/L with marked increases in total acidity and

buffering power. The addition of gypsum initially produces a significant increase in sulfate and calcium concentrations, although calcium decreases appreciably in the first 2 months. The addition of tartaric acid leads to a marked reduction in potassium concentrations because of the induced precipitation of KHT. The combined addition of gypsum and tartaric acid produces an additive effect when compared to the doses of each one individually and this allows a reduction in the doses of tartaric acid necessary to achieve a pH of enological interest. Consequently, it has been verified that in warm regions it is possible to use both acidifiers in combination to reduce pH accurately. Lower amounts of tartaric acid, which is much more expensive than gypsum, can be used and the levels required are closer to the legal limits. Chemical modeling in which tartaric acid is considered to be monoprotic has shown excellent pH predictions for the effects of gypsum and tartaric acid in all cases, except when high doses of tartaric acid are combined with gypsum. Finally, it can be concluded that the use of gypsum is still of great interest for must acidification in warm regions.

## References

- Boulton, R. (1980). The general relationship between potassium, sodium and pH in grape juice and wine. *American Journal of Enology and Viticulture*, 31(2), 182–186.
- Casas Lucas, J. F. (2008). *The winemaking in Jerez in the XX century. Antecedents, interpretation and contributions 1955–1985*. Seville, Spain: Junta de Andalucía. Consejería de Agricultura y Pesca.
- e-CFR. Electronic Code of Federal Regulations. (2010). Title 27: Alcohol, Tobacco and Firearms PART 24 WINE Subpart I Storage, Treatment and Finishing of Wine § 24.246 Materials authorized for the treatment of wine and juice. Available on line at <<http://www.ecfr.gov/cgi-bin/text-idx?SID=5a39ba6737562446636a5b54a87b3961&node=27:1.0.1.1.19.12&rgn=div6#27:1.0.1.1.19.12.343.7>>, last accessed 12 April 2014.
- European Community. (1990). Council Regulation (EEC) N° 2676/90 determining the Community analysis methods applicable in the wine sector. *Official Journal of the European Community*, vol. L272, pp. 1–192.
- European Community. (2008). Council Regulation (EC) N° 479/2008 on the common organisation of the market in wine. *Official Journal of the European Union*, vol. L148, pp. 1–61.
- European Community. (2009). Commission Regulation (EC) N° 606/2009 laying down certain detailed rules for implementing Council Regulation (EC) N° 479/2008 as regards the categories of grapevine products, oenological practices and the applicable restrictions. *Official Journal of the European Union*, vol. L153, pp. 1–59.
- Fernández de Bobadilla, G., Quirós, J. M., & Serrano, J. J. (1954). The plastering of musts. *Journal of the National Institute of Agronomic Research (INIA)*, 31, 411–416.
- Frayne, R. (1986). Direct analysis of the mayor organic components of grape, must and wine using high performance liquid chromatography. *American Journal of Enology and Viticulture*, 37, 281–287.
- Gomez Benitez, J., Grandal Delgado, M. M., & Diez Martin, J. (1993). Study of the acidification of Sherry musts with gypsum and tartaric acid. *American Journal of Enology and Viticulture*, 44(4), 400–404.
- Gonzalez-Gordon, M. M. (1972). Sherry. The Noble Wine.
- Harris, J. M., Kriedermann, P. E., & Possingham, J. V. (1971). Grape berry respiration: Effects of metabolic inhibitors. *Vitis*, 9, 291–298.
- Jeffer, J. (1982). *Sherry* (3rd ed.). London: Faber and Faber.
- Moreno Vigar, J., & Peinado Amores, R. A. (2010). *Oenological Chemistry* (1st ed.). San Diego CA. (USA): Academic Press.
- Pato, M. A. S. (1971). Use of plaster for acidity correction in musts and wines. *De Vine et vino Portugaliae Documenta, Serie II Enology*, Vol. 5(N° 5). Lisbon: National Center of Vine and Wine Studies.
- Plane, R. A., Mattick, L. R., & Weirs, L. D. (1980). An acidity index for the taste of wines. *American Journal of Enology and Viticulture*, 31(3), 265–268.
- Plinius Maior. (1st Century). *Naturalis historiae*, Book XIV, Chapter XIX.
- Prenceti, E., Toso, S., Daniele, P. G., Zelano, V., & Ginepro, M. (2004). Acid-base chemistry of red wine: Analytical multi-technique characterisation and equilibrium-based chemical modelling. *Analytica Chimica Acta*, 507(2), 263–273.
- Prenceti, E., Berto, S., Toso, S., & Daniele, P. G. (2012). Acid-base chemistry of white wine: Analytical characterisation and chemical modelling. *ScientificWorldJournal*.
- Ribereau-Gayon, P., Dubourdieu, D., Doneche, B., & Lonvaud, A. (2006). *Handbook of Enology. Vol. 1. The microbiology of wine and vinifications* (2nd ed.). Chichester: John Wiley & Sons.
- Ruffner, H. P., Brem, S., & Rast, D. M. (1983). Pathway of photosynthetic malate formation in *Vitis vinifera*, a C3 plant. *Plant Physiology*, 73, 582–585.
- Shimazu, Y., & Watanabe, M. (1981). Studies on organic acids in grape must and wine. III. Effects of yeast strains and environmental conditions on formation of organic acids in must during fermentation. *Journal of Fermentation Technology*, 59(1), 27–32.
- Sturm, M. E., Arroyo-López, F. N., Garrido-Fernández, A., Querol, A., Mercado, L. A., Ramirez, M. L., et al. (2014). Probabilistic model for the spoilage wine yeast *Dekkera bruxellensis* as a function of pH, ethanol and free SO<sub>2</sub> using time as a dummy variable. *International Journal of Food Microbiology*, 170, 83–90.
- Usseglio-Tomasset, L. (1995). *Chimica Enologica*. Brescia, Italy: Ed. AEB.